# IN SITU THERMAL REMEDIATION: MECHANISMS, PRINCIPLES AND CASE STUDIES

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## Introduction

Since the early 1990's, thermal methods of enhanced oil recovery have been adapted for the remediation of soils and groundwater. Steam injection and electrical resistance heating have proven to be robust and aggressive techniques for the enhanced recovery of volatile and semivolatile organic compounds from a variety of geologic settings. The reason for the wide applicability of these technologies to various contaminants and geologies is the large number mechanisms that increase the mobility of contaminants as the temperature is increased. In order to understand the applications of these technologies and their effectiveness, the mechanisms for enhanced recovery that are important in a given situation must be understood. This presentation first covers the important mechanisms in thermal remediation, then gives an overview of the application of steam injection and electrical resistance heating technologies. Also, brief summaries of a steam injection demonstration into fractured bedrock at Loring Air Force Base and an ERH pilot study at the Silresim Superfund Site are presented. Other thermal remediation technologies, such as hot water injection and conductive heating, have also been successful in certain applications. This presentation will focus on the steam injection and electrical heating as they are the most widely applicable.

## Mechanisms in Thermal Remediation

All of the physical properties of organic liquids that effect fluid flow in the subsurface – density, viscosity, vapor pressure, and aqueous solubility – are all temperature dependent (Davis, 1997). The changes that these properties undergo as the temperature increases all enhance the mobility of the organic liquid in the subsurface, and thus our ability to recover them. For volatile organic compounds, which includes jet fuels and chlorinated solvents, the most important mechanism for enhanced recovery using thermal methods is the increase in vapor pressure with temperature. Vapor pressure increase exponentially as a function of temperature, greatly enhancing recovery in the vapor phase. Steam distillation occurs when there is a nonaqueous phase liquid present as well as water. When the combined vapor pressures of the water and liquid equals the local ambient pressure, than boiling will occur. Thus NAPLs in the subsurface will boil at temperatures less than steam temperatures, and can be recovered rapidly. Once the NAPL is recovered, steam stripping will preferentially remove the dissolved phase contaminants from the groundwater, and dissolved phase concentrations can be reduced by orders of magnitude with relatively small inputs of energy.

Many semivolatile compounds, such as heavy fuels, are viscous liquids which contain a mixture of high and low boiling hydrocarbons. In these cases, using heat to reduce the viscosity of the liquid and recovering the liquid phase will allow the recovery of more of the high boiling compounds, as well as the low boiling constituents. Viscosity decreases exponentially as the temperature is increased, and a fuel that has a high viscosity at ambient temperatures may be made 5 to 10 times more mobile by raising the temperature to 50 - 60C. Beyond that temperature, further decreases in viscosity are generally small. For viscous liquids, the viscosity reduction may be the most important mechanism for enhanced recovery in thermal remediation.

In addition to these major mechanisms for the two different types of organic liquids, dissolved phase concentrations are also expected to increase substantially during thermal remediation due to increased solubilities and dissolution rates, greatly increasing the amount of contaminants that can be recovered in the aqueous phase. Biodegradation has been shown to still be active at thermal remediation temperatures for some types of contaminants (Newmark and Aines, 1995), and the higher temperatures also increase the rates of some oxidation or hydrolysis reactions. Thus, a variety of mechanisms act together to mobilize or destroy contaminants during thermal remediation.

## Steam Injection for Remediation

Steam injection has an additional mechanism that can be very effective for the recovery of liquids: displacement (Davis, 1998). Generally this technology is applied by surrounding the NAPL zone by injection wells and displacing all of the contaminants to central extraction wells. Contaminants are recovered as a separate phase liquid, in the aqueous phase, and in the vapor phase, with the proportion in each phase dependent on the thermodynamic properties of the contaminants. Steam injection remediation is favorable when the bulk permeability is moderate to high (greater than $5 \times 10^{-5}$ cm/sec), low permeability layers are less than two meters in thickness, and for deeper depths of remediation. Although steam will preferentially flow into higher permeability layers, low permeability layers will be heated by conduction. If the low permeability layers are less than about two meters, they can be heated to steam temperatures during the typical treatment time of a thermal remediation.

Designing and operating a successful steam injection remediation requires an understanding of how steam behaves in the subsurface, the properties of the contaminant, and the geology and hydrogeology of the system in order to get heat to where it is needed and to capture the mobilized contaminants. The potential for downward migration of DNAPLs during a steam injection can be mitigated by creating a hot floor under the area to be treated, and/or by coinjecting air with the steam to avoid the formation of a DNAPL bank. Cyclic steam injection with continuous liquid and vapor extraction creates pressure gradients within the system that enhances the vaporization of contaminants. Steam injection into soils and aquifers has successfully recovered volatile contaminants including chlorinated solvents, fuels such as gasoline and diesel, and heavier polycyclic aromatic hydrocarbons such as creosote. For many soil and aquifer systems where volatile contaminants are to be recovered, steam injection may be considered routine. Current areas of research related to steam injection includes mechanisms that enhance liquid phase contaminant recovery, chemical reactions at thermal remediation temperatures, and the use of the technology in complex geologic settings such as fractured bedrock.

## Steam Injection Demonstration in Fractured Bedrock

In 2002, two steam injections into fractured bedrock were conducted, one at Edwards AFB (California) and the other at the former Loring AFB (Maine). At the former Loring AFB, a Technical Impractibiltiy (TI) wavier has already been issued for the groundwater at the former Quarry site due to the presence of chlorinated solvents DNAPL from the past disposal of leaky drums. The steam injection demonstration was undertaken at the request of the State of Maine Department of Environmental Protection (DEP) as a research project on the recovery of DNAPL from fractured rock. The demonstration was a joint project by the Air Force, EPA Region I, Maine DEP, EPA SITE program, and SteamTech Environmental Services. Characterization was done during the summer of 2001 and 2002. Rock chip and groundwater samples taken prior to the demonstration showed that PCE was the main contaminant present in this site, at concentrations ranging up to 130 mg/kg in rock fracture surfaces and 8800 micrograms/liter in groundwater samples. Development of the fracture framework from rock cores and borehole geophysical data showed a very complex geology of sparsely fractured rock, dominated by three sets of fractures. Hydraulic testing showed that the site has generally low permeability, with most of the permeability concentrated at about the depth of the water table. Interconnectivity testing did not indicate that all of the areas of the site were interconnected with the borehole system in place. The highest contaminant concentrations were found where fractures apertures decreased, yielding very little or no permeability. Rock chip samples taken of the matrix at various distances from fractures showed that the contaminants occur within about a foot of the fracture surfaces.

Based on the results of the characterization activities, a steam injection and extraction system was designed. After steam injection was initiated, injection rates and contaminant extraction rates were monitored at each well. Additional steam injection was then initiated into wells that were not producing significant amounts of contaminants. Steam injection with continuous extraction of liquids and vapors occurred for 82 days, with an additional 7 days of liquid and vapor extraction afterwards. Effluent liquid and vapor samples were collected daily throughout the demonstration. About 20 days into the steam injection, increases in effluent concentrations of volatile organic compounds (VOCs), diesel range organics, and gasoline range organics in both the aqueous and vapor phases were observed, and the concentrations continue to slowly increase throughout the remainder of the demonstration. Peak concentrations were two to three orders of magnitude greater than the initial concentrations. At the time that the concentrations began to increase, only small temperature increases were observed at any of the thermocouple locations, and none of the extraction wells showed any increase in temperature. Approximately 70 days of steam injection were required before a small temperature increase was observed at any extraction well. Electrical resistance tomography, which was used to track the injected fluids and temperature changes, seemed to show changes in electrical resistance along fracture planes and fracture intersections. Post treatment rock and groundwater samples will be collected in the Spring of 2003.

### Electrical Resistance Heating Remediation

ERH, also called Six Phase Soil Heating, or Joule heating, also has its roots in enhanced oil recovery. Electrodes are inserted into the ground in hexagonal or triangular arrays, and different phases of three phase or six phase electricity is applied to the electrodes. Current is carried away from the electrodes by water in the pore spaces, but the natural resistance to electrical current flow of the soil causes the loss of energy as heat. Thus, the technology requires the presence of water at saturations of at least about three percent, which limits the temperatures that can be achieved with this technology to the boiling point of water. The presence of ions in clay layers increases the current flow and thus the heat deposition in low permeability zones. Volatile contaminants are vaporized, and collected by soil vacuum extraction (SVE) which is applied at the electrodes and through additional wells in the vadose zone. The technology has been successfully used both above and below the water table, and has been successful in low permeability materials where it is difficult if not impossible to inject fluids. Recently the technology was expanded by its use in a waste pit which contained buried metal objects, and was successful in removing VOCs from a liquid waste that was a mixture of a large number of organic chemicals.

### Silresim Superfund Site ERH Pilot Test

Subsurface soils and groundwater beneath the Silresim Superfund site contains a mixture of spent solvents due to past disposal practices and spills. Previous pilot scale SVE systems collected significant amounts of contaminants, but it was determined that the SVE system could not reach site goals in a reasonable time frame. An ERH pilot test was undertaken to determine if this technology could improve the recovery of contaminants and to determine if engineering solutions could be found to the potential interferences of site infrastructure and other above ground systems to allow the technology to be used safely at this site. A hexagonal array with a central neutral electrode was installed in a highly contaminated area of the site adjacent to metal fencing and other above ground systems. Wire mesh on the ground surface dispersed stray current and maintained the step potential at less than 15 volts. The 30 foot diameter array was heated by approximately 285,000 kW-hr of energy over 70 days. Vapors were extracted from each of the electrodes and from horizontal wells in the vadose zone. At the completion of the pilot, groundwater concentrations in the shallow interval in the center of the array showed a greater than 99.6% decrease, going from 655 ppm to 2.3 ppm. Most of the remaining contaminant was acetone. The deeper portion of the treatment zone showed a 94 percent reduction in contaminant concentrations, while the ten foot zone directly beneath the treatment zone showed a 66 percent decrease in concentrations. These results show very good removal of contaminants and no indication of downward migration of contaminants during the remediation. An estimated1400 pounds of chlorinated solvents and fuel components were recovered. Post treatment soil and groundwater samples are currently being recovered.

### References

Davis, E. L., How heat can enhance in-situ soil and aquifer remediation: Important chemical properties and guidance on choosing the appropriate technique, Ground Water Issue Paper, US Environmental Protection Agency, EPA/540/S-97/502, April 1997.

Davis, E. L., Steam injection for soil and aquifer remediation, Ground Water Issue Paper, US Environmental Protection Agency, EPA/540/S-97/505, January 1998.

Newmark, R. L., and R. D. Aines, Summary of the LLNL gasoline spill demonstration - Dynamic Underground Stripping Project, Lawrence Livermore National Laboratory, Berkeley Environmental Restoration Center, UCRL-ID-120416, April 3, 1995.